A LANDMARK PAPER ON CARBON-SUPPORTED CATALYSTS: THE REAL STORY REVEALED BY THE SCIENCE CITATION INDEX

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INTRODUCTION

In the 1980's there was a resurgence of interest in understanding carbon as a catalyst support. It had been well documented by then that high catalyst dispersion can be achieved on carbon supports under certain conditions. This was attractive because it had also been established that carbon-supported hydrotreatment catalysts are much less prone to deactivation by coke deposition than the conventional alumina-supported catalysts. At Penn State, conditions were ideal to fully understand the virtues of carbon-supported catalysts and to rationalize the potential pitfalls in their preparation. Frank Derbyshire had just arrived from Mobil R&D and, being an expert in coal hydroprocessing, was eager to renew his studies on the catalytic properties of carbon. Alan Scaroni had been conducting an extensive study of coking propensities of carbon and alumina. And there was also the support of Phil Walker, with his encyclopedic knowledge of carbon materials and pioneering expertise in their use as catalyst supports.

Prior work had shown that "catalyst activity is strongly influenced by the interaction between the carbon surface and the deposited metal species" [1]. However, the exact nature of this influence was not clear [2]. Therefore, Derbyshire and his collaborators set out to "investigate the importance of surface functional groups on [sic] the activity of carbon-supported MoS_2 catalysts" [1]. In contrast to much of the previous work, in which "the carbons used ... were of different origin and varied in their chemical structure, textural properties and content of impurities," in this study "a single metal salt precursor and a single parent carbon were selected."

Offered below is a summary of the seminal importance of this study, even though its findings and conclusions, seen in hindsight, were somewhat ambiguous. While necessarily subjective, such an account is not only appropriate as a contribution to the symposium in memory of Frank Derbyshire but arguably also as a record of equal value (if not greater) as the more "objective" accounts offered by scientometricians or historians of science. Historians of science typically direct their efforts only at the "big stories," thus leaving us ignorant of the instructive historical context of "everyday science," where wheel reinventions are much more common. The Citation Index, an increasingly popular and potentially powerful tool, is too often used only by librarians and science administrators, as an end in itself rather than the means toward a more incisive analysis of the impact of a scientific publication.

HIGHLIGHTS OF "THE INFLUENCE OF SURFACE FUNCTIONALITY ON THE ACTIVITY OF CARBON-SUPPORTED CATALYSTS" [1]

Figure 1 reproduces the key results of this study. A "somewhat hydrophobic" polymer-derived carbon was subjected to widely varying oxidizing (a) and nitriding (b) treatments prior to their incipient wetness impregnation with ammonium heptamolybdate dissolved in a mixture of 90% H_2O/10% ethanol. Catalytic activity was determined at 450 °C by monitoring asphaltene conversion in batch hydrogenation tests of a process-derived coal liquefaction solvent. The extent of coke formation was determined by monitoring the weight gain of the catalyst after reaction. The effectiveness of carbon pretreatment was analyzed by elemental analysis and FT infrared spectroscopy. Maximum oxygen incorporation occurred when the carbon was treated in conc. HNO_3 and H_2SO_4 (ca. 25.3 and 20.1% O, respectively, vs. 1.4% in the parent carbon); nitrogen content increased from <0.05 to 0.53 and 0.87% after NH_3 treatment at 400 and 600 °C, respectively.

In contrast to the unclarified and largely detrimental effects of carbon oxidation, nitriding "was found to have a distinct effect in enhancing catalyst activity," and the authors proposed that this is because "nitrogen-containing surface groups ... provide preferential sites for the adsorption of Mo species." Even though the authors did not identify these sites, they argued prophetically that "the affinity between a particular carbon surface and the [selected catalyst] precursor will depend upon the compatibility of the two chemical structures."

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IMPACT OF "THE INFLUENCE OF SURFACE FUNCTIONALITY ON THE ACTIVITY OF CARBON-SUPPORTED CATALYSTS" [1]

The story told by the Science Citation Index (Institute of Scientific Information, Philadelphia, PA), as of June 2000, is summarized in Figure 2. Not a widely cited paper, one would conclude, but such a conclusion would be a misleading one. As emphasized by Radovic and Rodríguez-Reinoso [2], this was the "first explicit attempt to clarify the influence of surface functional groups on the activity of carbon-supported catalysts." Intriguingly, however, most of the (non-self-) citing studies listed in Figure 2, even some of the most recent ones, do not identify it as such. Instead, the context of most citations is arguably peripheral and too often simply wrong.

(a) Inspired by Ref. 1, Guerrero-Ruiz et al. [3] performed a similar study of the role of nitrogen and oxygen surface groups in the behavior of carbon-supported iron and ruthenium CO hydrogenation catalysts, with ambiguous results.

(b) Abotsi and Scaroni [4-6] further pursued the issues raised in Ref. 1, emphasizing that "the activities of carbon-based catalysts are dependent on the nature and concentration of carbon surface functional groups." In particular, they were among the first investigators to appreciate [5] the crucial role of carbon surface charge [2]. Unfortunately, they mixed up the conditions of development of surface charge: it is the positively charged carbons, and not negatively charged ones (see p. 110 in Ref. [5]) that "are generally produced at high temperatures," and this turned out to be one of the keys to the preparation of highly dispersed molybdenum catalysts using anionic precursors [2, 7, 8].

(c) Groot et al. [9] echoed the underlying theme in Ref. 1, that chemical treatments should create catalyst anchoring sites on the support surface, and argued that "carbon blacks have a low density of functional (oxygen-containing) groups," which might serve as such sites.

(d) García and Schobert [10] mention Ref. 1 in passing, as a study of "hydrodesulfurization of thiophenes" [sic]. In a subsequent study by the same group [11], Ref. 1 is again miscited as a study in which, presumably, "limits [in achievable liquefaction conversion] have been observed beyond which further increases in Mo addition no longer have a significant effect."

(e) The study of Solar et al. [7] is a direct descendant of Ref. 1, and its success in providing some of the key answers regarding the role of carbon surface chemistry [2] was largely due to the fact that Ref. 1 had asked the right questions. The studies by Suh et al. [12], Martín-Gullón et al. [13], Kim et al. [14], Jansen and van Bekkum [15], Krishnankutty and Vannice [16], Bastl [17], Dandekar et al. [18], Vázquez et al. [19] and Aksoylu et al. [20] fall into the same category. In a recent study, de la Puente and coworkers [21, 22] revisited the topic of the interaction between Mo and activated carbons, did cite Ref. 1 in the appropriate context, but failed to recognize that the key issues had been largely resolved in the intervening period [2]. Disregarding the fact that adsorption of molybdate anions is suppressed by carbon oxidation, largely because of the presence of acidic functional groups (e.g., COOH), these authors concluded, rather paradoxically, that "acidic groups were acting as chemical anchorage centers." It is not clear how "oxygenated surface groups ... can act as chemical anchorage sites for molybdate ions." They argued that "[w]hen using incipient-wetness impregnation, electrostatic repulsions seem to be less important than other factors such as the hydrophilicity of the sample and the distribution of oxygen-containing surface groups;" they did not provide measurements of catalytic activity to support these interesting claims.

(f) Klinik and Grzybek [23] cite Ref. 1 as, presumably, a study which has shown that "the effect of oxidation [of carbon using concentrated HNO_3] depends on the structure of the starting material. A subsequent study by the same senior author [24] uses Ref. 1 to support the argument that "some bigger pores (macropores)" are formed during oxidation of an activated carbon.

(g) In what is perhaps the most intriguing one of all the inappropriate citations, Sakanishi et al. [25] invoke Ref. 1 after saying that "fine particles of a Mo-based catalyst are applied in a moving bed." Along the same lines, Mochida and Sakanishi [26] further invoke Ref. 1 in vain by saying that "titania and carbon have recently been examined as supports for iron and Ni-Mo sulfides."

Many other studies, especially in the 1990s, had as their *main* theme the effect of surface chemistry on the dispersion and activity of carbon-supported catalysts, and they are the ones that should have given, but did not, due credit to the pioneering effort of Derbyshire and his colleagues. Several examples will be provided during the presentation.

SUMMARY

Figure 3 is an attempt to synthesize our collective knowledge of the influence of surface functionality on the activity of carbon-supported catalysts. Its roots can be traced to the incisive questions posed by Frank Derbyshire and his colleagues in Ref. 1, as well as to improved understanding of "the compatibility of the two chemical structures" [1]. Apart from the effects of wetting and pore size distribution, carbon surface functionality governs the extent of adsorption of the catalyst precursor and the extent of its reduction or conversion to active state. Thus, for example, in catalyzing the oxygen transfer reactions illustrated here, the optimum surface chemistry is the one that (a) provides the anchoring sites for the catalyst precursor (e.g., carboxyl groups for ion exchange with cationic precursors), (b) allows favorable electrostatic interaction between the support and catalyst precursor (e.g., adsorption of anions at a pH less than the point of zero charge of the carbon), (c) prevents excessive catalyst mobility on the support surface, and (d) also facilitates the achievement of an intermediate oxidation state of the active phase, which in turn promotes oxygen transfer from the gas phase to the carbon surface.

The two-tiered value of the Science Citation Index to researchers, as opposed to librarians and research administrators, has been demonstrated here. On one hand it provides a quick start in the evaluation of scientific impact of a peer-reviewed publication. On the other hand, its increased use along the lines suggested here will hopefully force us all to be more careful, more selective and more responsible in collecting the lists of references for our publications. Perhaps sometime soon this important, yet too often neglected, activity will again be regarded as an opportunity to give credit where credit is really due and not as a matter of convenience, tradition and even nuisance. Had this been the case with Ref. 1, its "objective impact" would have been much closer to the admittedly subjective but arguably more appropriate evaluation presented here.

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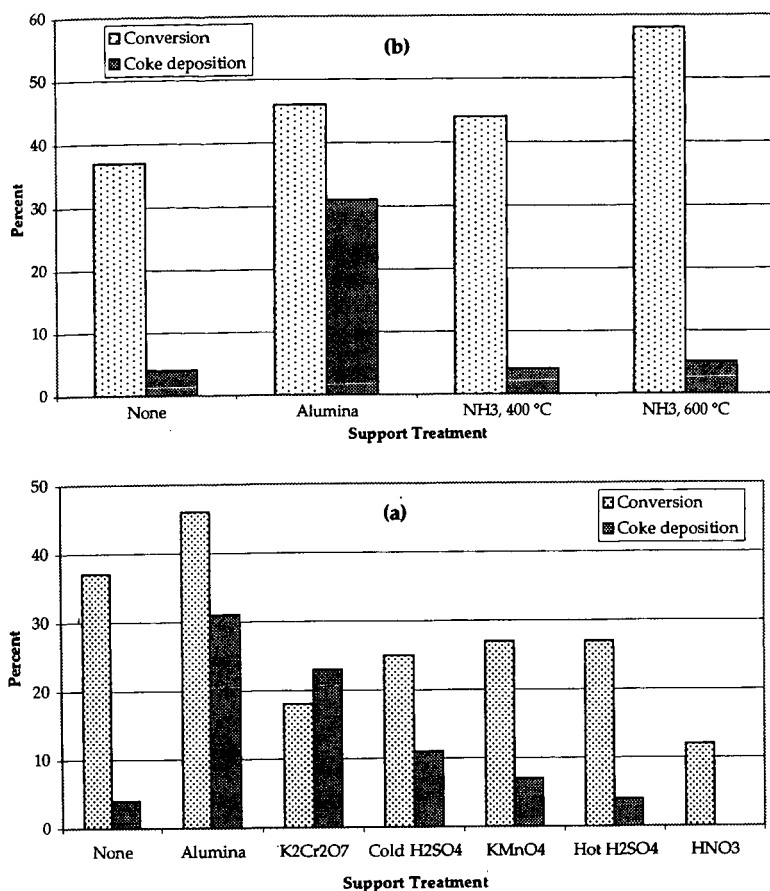26. Mochida, I. and K. Sakanishi, *Adv. Catal.*, 1994. 40: p. 39.

FIGURE 1. Effect of carbon surface functionality on the performance of sulfided Mo/C catalysts: (a) oxidative treatments; (b) nitriding treatments (from Ref. 1).
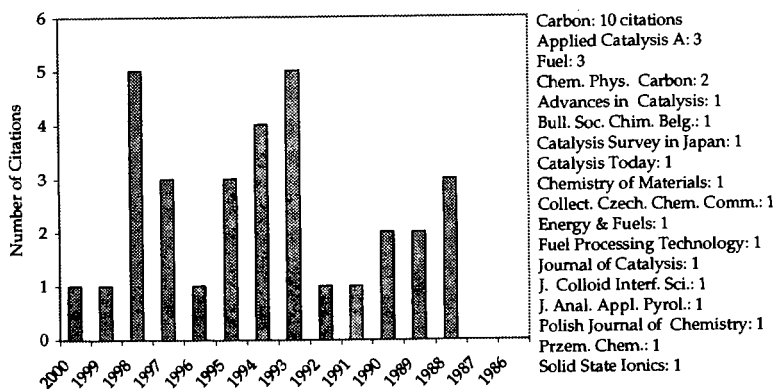

Carbon: 10 citations
Applied Catalysis A: 3
Fuel: 3
Chem. Phys. Carbon: 2
Advances in Catalysis: 1
Bull. Soc. Chim. Belg.: 1
Catalysis Survey in Japan: 1
Catalysis Today: 1
Chemistry of Materials: 1
Collect. Czech. Chem. Comm.: 1
Energy & Fuels: 1
Fuel Processing Technology: 1
Journal of Catalysis: 1
J. Colloid Interf. Sci.: 1
J. Anal. Appl. Pyrol.: 1
Polish Journal of Chemistry: 1
Przem. Chem.: 1
Solid State Ionics: 1

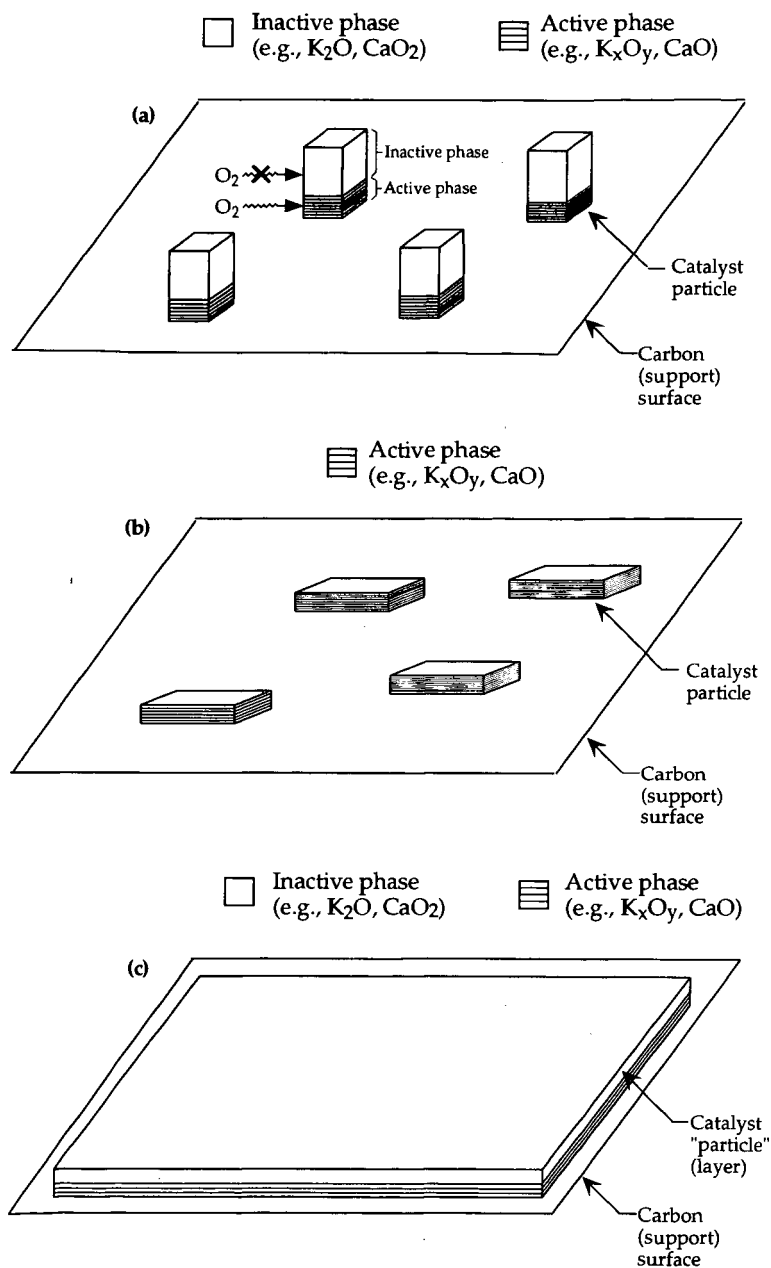**FIGURE 2.** Summary of the Citation Index search for Ref. 1, as of June 2000.

FIGURE 3. Summary of the influence of carbon surface functionality on the dispersion (and thus catalytic activity) of carbon-supported catalysts: (a) intermediate dispersion (activity); (b) high dispersion (activity); (c) low dispersion (activity).